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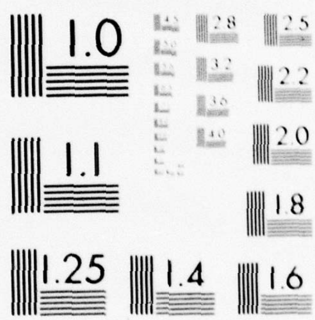

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The heavy atom effect in triplet 9,10-dichlorophenanthrene and 1,2,3,4-tetrachloronaphthalene is investigated by PMDR techniques. As in the parent hydrocarbons, spin-orbit and spin-orbit vibronic mechanisms are invoked to explain the results. The relative radiative rates of the triplet zero-field levels are determined by static distortions of the chlorine atoms, while the intersystem crossing rates from $S_{(1)}$ are mainly governed by the enhancement of spin-orbit vibronic coupling via C-Cl out-of-plane modes that mix the relevant σ,π^* and π,π^* states. In both processes the top two levels (τ_A and τ_B) are more active, with τ_B the most favoured of the two.

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Tau(A) and Tau(B)

The Study of the Intramolecular Heavy Atom Effect in 9,10-Dichlorophenanthrene and 1,2,3,4-Tetrachloronaphthalene Using PMDR Techniques

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ABSTRACT

The heavy atom effect in triplet 9,10-dichlorophenanthrene and 1,2,3,4-tetrachloronaphthalene is investigated by PMDR techniques. As in the parent hydrocarbons, spin-orbit and spin-orbit vibronic mechanisms are invoked to explain the results. The relative radiative rates of the triplet zero-field levels are determined by static distortions of the chlorine atoms, while the intersystem crossing rates from S_1 are mainly governed by the enhancement of spin-orbit vibronic coupling via C-Cl out-of-plane modes that mix the relevant σ,π^* and π,π^* states. In both processes the top two levels (τ_A and τ_B) are more active, with τ_B the most favoured of the two.

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1. Introduction:

It is well known that the internal heavy atom effect (HAE) on the dynamic properties of triplet aromatic molecules exhibits itself by enhancing multiplicity forbidden transitions via increased spin-orbit coupling routes with singlet states. $^1\sigma,\pi^*$ states play the most prominent role in this scheme since coupling between $^1\pi,\pi^*$ and $^3\pi,\pi^*$ states is vanishingly small (1-3). Experimentally, an enhanced $S_1 \rightarrow T_1$ intersystem crossing rate, a shortening of the T_1 lifetime and an increased $T_1 \rightarrow S_0$ radiative decay are associated with the HAE (4). Considerations of the phosphorescence polarization and the anisotropy of the dynamic behaviour of individual zero-field levels of T_1 in haloaromatics require the involvement of spin-vibronic and spin-orbit vibronic interactions (5-7).

The use of PMDR techniques (3) has proven to be a powerful tool for investigating the dynamics of individual zero-field level behaviour. The radiative properties of the three levels for the 0-0 optical transitions have led to predictions concerning static molecular distortions (8,9) in haloaromatics as well as assignments of the orbital symmetries of T_1 in benzene (10), phenanthrene (11), naphthalene (12) and tetrachlorobenzene (13). Furthermore, the radiative properties of the zero-field levels observed by monitoring vibronic bands together with their relative intersystem crossing rates (12,14-16) established the importance of out-of-plane vibrational modes in the spin-orbit vibronic coupling scheme.

Recently, the dynamic properties of the triplet state of various haloaromatic compounds were studied (17). In this paper we report similar results for 9,10-dichlorophenanthrene (DCP) and 1,2,3,4-tetrachloronaphthalene (TCN) in n-hexane at 1.6°K. Experimental techniques have been thoroughly described in the literature (3,18-22), and will not be discussed here.

2. Results:

2.1.1. 9,10-Dichlorophenanthrene:

The uncorrected 1.5°K phosphorescence spectrum is shown in Fig. 1 while the calibrated (using Hg lines) band locations are given in Table 1. Two sites, 82 cm^{-1} apart, are observed with 0-0 bands at 20842 and 20760 cm^{-1}, respectively. The two sites are also observed in the 0-260 cm^{-1} vibrational bands. The stronger 0-0 band (20760 cm^{-1}) was monitored throughout the experiment. The zero-field transitions (D-E and 2E) that are shown in Table 2 are close to those known for phenanthrene. The 2E transition monitored at 20760 cm^{-1} is slightly different from that at 20842 cm^{-1}, thus confirming the existence of two sites. The D+E transition can only be observed in EEDOR (23). The relative radiative rates k_i^r (0-0), the lifetimes τ_i, the relative populating rates, K_i, and the relative populations, N_i, are also shown in Table 2. For comparison purposes, results for phenanthrene found in the literature (11,15) are included.

2.1.2. 1,2,3,4-Tetrachloronaphthalene:

The phosphorescence spectrum and calibrated bands for TCN are shown in Fig. 2 and Table 3, respectively. The zero-field transition energies (also presented in Fig. 2) are typical of naphthalene and azanaphthalene systems. Table 4 gives the dynamic properties. These are compared with naphthalene results (12, 15), and it is noticed that TCN follows the same general trends as in the parent hydrocarbon.

3. Discussion:

3.1. Relative radiative rates:

In both chlorinated molecules it is observed that τ_B (total symmetry = spin(A_2) x orbital(B_2) = B_1) is the most radiative level in the 0-0. This is also the case for the parent hydrocarbons. The group theoretical predictions of spin-orbit coupling (SOC) in C_{2v} symmetry (see ref. 3) confirm that this level is the one that mixes with the $^1\sigma,\pi^*$ states ($^1B_1$) and hence benefits most from spin-orbit coupling. The lowest level, τ_N, mixes with the $^1\pi,\pi^*$ states ($^1A_1$) and hence is the least emissive. Similar arguments indicate that the orbital symmetry of the lowest triplet state of TCN and DCP is of B_2 species, since otherwise τ_A would be the most radiative level; if the orbital symmetry were A_1, then τ_A would have total symmetry B_1 and it would mix with the $^1\sigma,\pi^*$ (B_1) state. Comparison of DCP with phenanthrene shows that the level τ_A is emissive in the substituted compound though the parent molecule doesn't show such activity. This can be explained by static in-plane distortion of the two chlorine atoms in a manner that destroys the C_2 and reflection symmetry perpendicular to the plane of the molecule. This mixes the τ_B character into the τ_A level and causes the observed radiative activity of the τ_A. In TCN static out-of-plane distortions of the crowded chlorine atoms seem to be the cause of the radiative character of the lowest level τ_N, which is dark in naphthalene. Such behavior has also been observed for 2,3-dibromonaphthalene (8).

3.2. Intersystem Crossing Rates:

The trend in the relative intersystem crossing rates shows the same behavior for the DCP and TCN as for the parent hydrocarbons. The top two levels, τ_A and τ_B, are most favoured with τ_B having the higher rate of the two. As in the parent hydrocarbons (3, 15) the results can be explained by spin-orbit vibronic coupling (see refs. 3 and 15). Intersystem crossing from $S_1(^1\pi,\pi^*)$ to $T_1(^1\pi,\pi^*)$ is not favourable by SOC alone. Vibronic coupling via a_2 or b_1 vibrations could contaminate the $S_1(^1B_2)$ with $^1\sigma,\pi^*$ character. The contaminated singlet has better SOC ability with the T_1 state. Alternatively the vibronic mixing could occur in the triplet manifold with exactly the same predictions. The a_2 vibration enhances level τ_A while the b_1 vibration enhances the population of τ_B (e.g., τ_A: $^3B_2 \xleftrightarrow{SOC} {}^1B_1 \xleftrightarrow{a_2} {}^1B_2$). However, compared to the parent hydrocarbons τ_B is even more favoured than τ_A. This indicates that the heavy-atom enhances the ability of the b_1 vibration to couple the electronic levels more than the a_2 mode. The π,π^* and σ,π^* states are orthogonal and possess different symmetries with respect to the molecular reflection plane. Thus the a_2 and b_1 modes are out-of-plane vibrational modes. Their enhancement by heavy atom substitution results in the enhancement of a strong nontotally symmetric progression in the phosphorescence spectrum. This has been observed at 77°K for various halophenanthrenes (30). Furthermore, in tetrachlorobenzene (TCB) (14) the most effective out-of-plane mode was found to be the b_{2g} which corresponds to C-Cl out-of-plane vibration. Thus, the active b_1 vibration in DCP and TCN can be safely assumed to be the out-of-plane C-Cl vibrations corresponding to the b_{2g} out-of-plane C-H or C-C bending vibration in naphthalene and the b_{2g} out-of-plane C-Cl vibration in TCB.

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Table 1. Calibrated phosphorescence bands of 9,10-dichlorophenanthrene

			$\Delta\nu(cm^{-1})$	
λ	cm^{-1}	Intensity*	Site I	Site II
4798	20842	M	0	
4817	20760	S		0
4861	20574	VW	268	
4875	20512	VW	330	
4881	20490	M		270
4896	20426	M	416	334
4899	20413	M	429	
4915	20346	M		414
4918	20334	M		426
4923	20313	VW	529	
4943	20231	W		529
4942	20236	W		
4996	20015	VW	827	
5000	20002	W	840	
5017	19932	W		828
5020	19922	M		838
5025	19900	VW	942	
5046	19819	VW		941
5047	19813	W	1029	
5069	19729	W		1031

*M = Medium; S = Strong; V = Very; W = Weak

Table 2. Zero-field transitions, the relative radiative rates, $k_i^r(0\text{-}0)$, the lifetimes, τ_i, and relative populations of the zero-field levels of 9,10-dichlorophenanthrene and phenanthrene (in parentheses)

	Phenanthrene*		9,10-Dichlorophenanthrene					
	$k_i^r(0\text{-}0)$	K_i	τ_i(sec)	$k_i^r(0\text{-}0)$*	K_i	N_i	2E	D-E
τ_A	0	0.70	0.48	0.46	0.60	0.43	2.864 (2.802)†	
τ_B	1	1	0.14	1	1	0.20		1.732 (1.731)†
τ_N	0.25	0.32	2.0	0	0.12	0.37		

*See Refs. 11,15

†M. A. de Groot and J. H. van der Waals, Physica 19, 1128 (1963).

Table 3. Calibrated phosphorescence bands of 1,2,3,4-tetrachloronaphthalene

Wavelength (Å)	Frequency (cm^{-1})	Relative Intensity	$\Delta\nu$ (cm^{-1})
5058	19770	VS	0
5100	19609	VW	161
5137	19466	W	304
5142	19448	M	322
5144	19440	S	330
5150	19418	M	352
5161	19377	M	393
5175	19324	MW	446
5200	19230	M	540
5217	19168	W	602
5234	19105	M	665
5239	19088	M	682
5256	19026	W	744
5262	19003	MW	767
5281	18937	W	833
5291	18901	W	869
5320	18799	W	971
5342	18720	W	1050
5372	18614	W	1156
5434	18402	W	1368
5440	18381	M	1389

Table 4. The dynamic properties of 1,2,3,4-tetrachloronaphthalene and naphthalene.

	Naphthalene (N)		1,2,3,4-tetrachloronaphthalene			
	$k_i^r(0\text{-}0)$ [a]	K_i [b]	τ_i(sec)	$k_i^r(0\text{-}0)$	K_i	N_i
τ_B	1	1	0.055	1	1	0.29
τ_A	0.25-0.22	0.39	0.200	0.13	0.25	0.26
τ_N	~ 0	0.17	1.50	0.13	0.05	0.45

a) Ref. 12. b) Ref. 15

FIGURE CAPTIONS

Fig. 1 9,10-dichlorophenanthrene phosphorescence spectrum (uncorrected) at 1.5° K in *n*-hexane. The axes system and the zero-field energy level diagram are also shown.

Fig. 2 Phosphorescence spectrum (uncorrected) at 1.5° K in n-hexane, energy level diagram, axis system and zero-field transitions (in GHz) of 1,2,3,4-tetrachloronaphthalene.

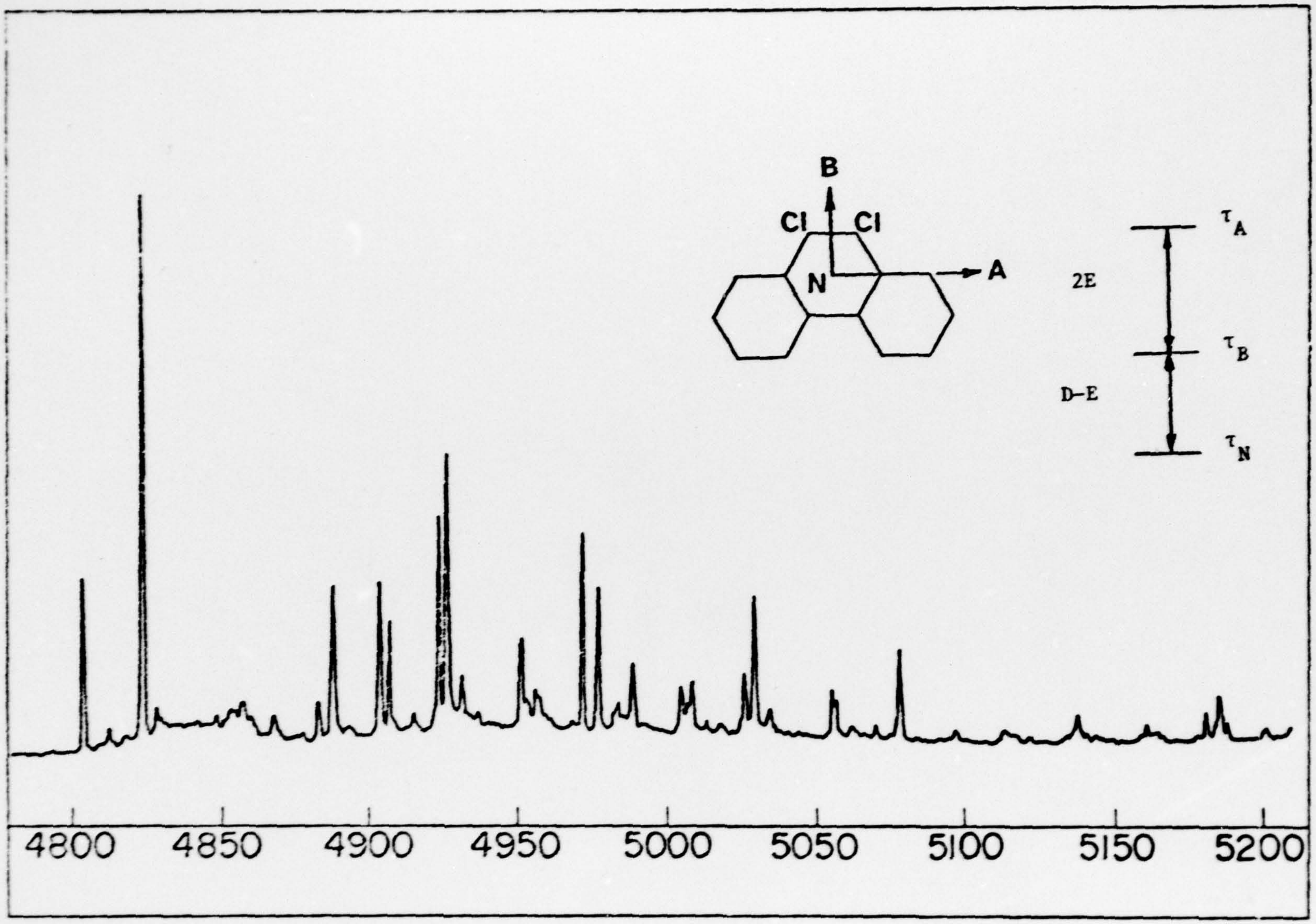
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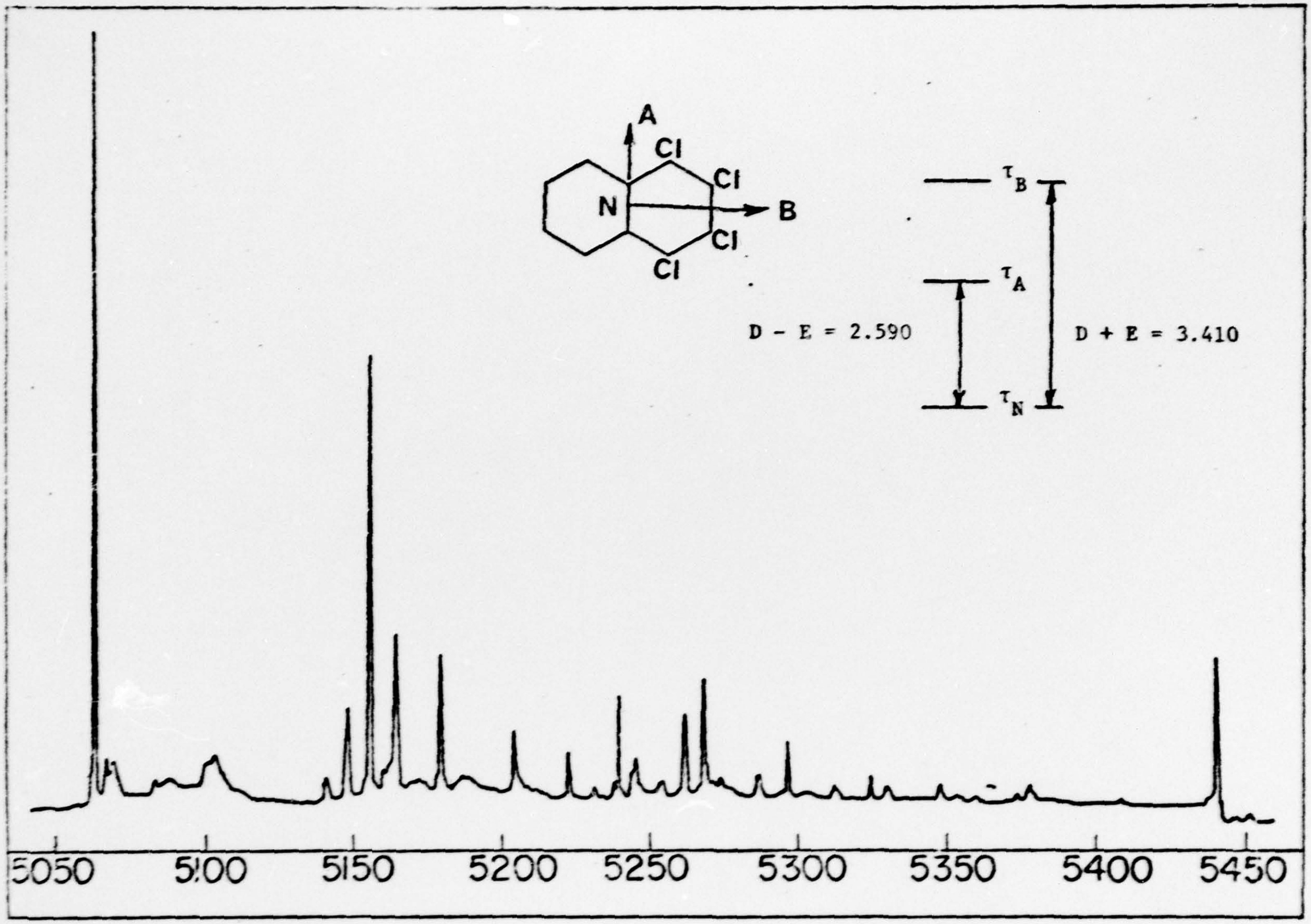
Fig 1



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D - E = 2.590
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Fig 2

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